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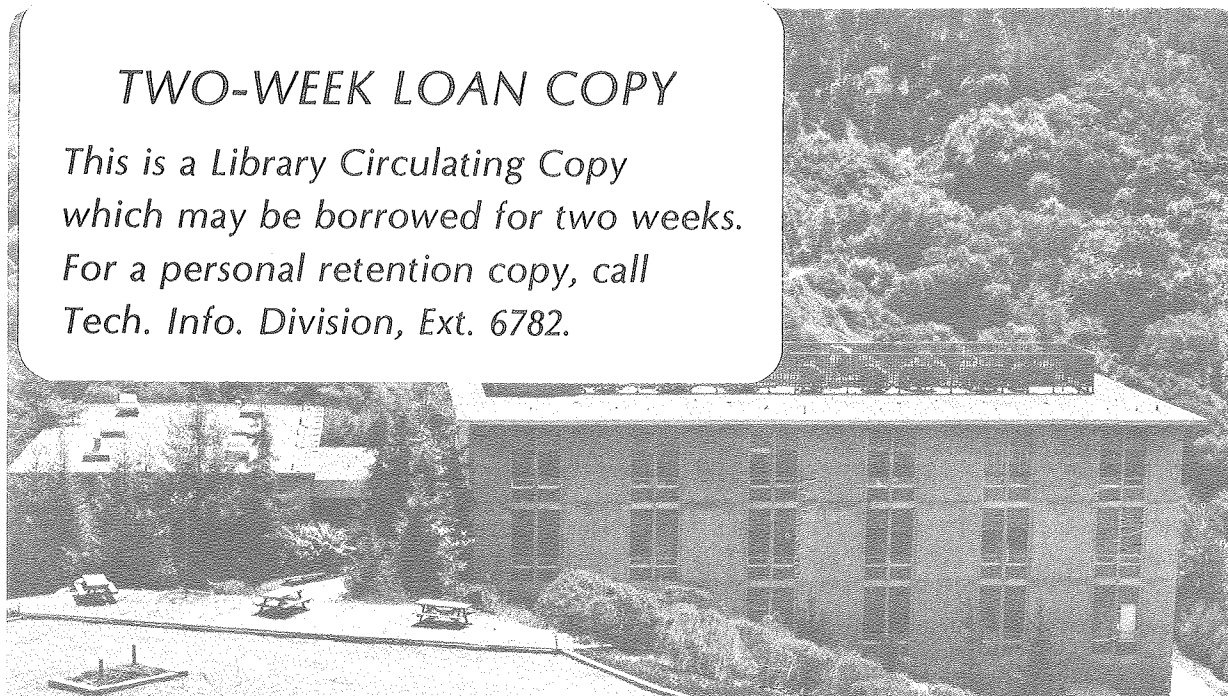
Materials & Molecular Research Division

RELATIVISTIC MODIFICATIONS OF COVALENT BONDING IN
HEAVY ELEMENTS: CALCULATIONS FOR TℓH

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October 1980

LBL-11611 c.2

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Relativistic Modifications of Covalent Bonding in
Heavy Elements: Calculations for TℓH

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Abstract

A test is presented of the proposal of Pyper that an
"orthogonal triplet bond" is an important factor in the
bonding of hydrogen to a very heavy element with a single
$p_{1/2}$ valence electron. The potential curve for TℓH was
calculated by relativistic quantum methods on two bases:
(a) excluding promotion of the $p_{1/2}$ spinor and allowing
the orthogonal triplet interaction and (b) allowing partial
promotion of the $p_{1/2}$ spinor by $p_{3/2}$ participation and
thereby approaching a normal sigma bond. The potential curve
for the normal sigma bond was also calculated by suppressing
the spin-orbit term. From these results and literature
information it is concluded that the orthogonal triplet
interaction makes no significant contribution to bonding.
Certain other aspects of the effect of relativity on bonding
are also discussed.

1. Introduction

Relativistic effects can result in substantial deviations from nonrelativistic expectations for chemical bonding where very heavy atoms are involved; this has been discussed in several recent reviews [1-3]. In the particular case of a single valence p-electron, e.g., thallium, the relativistic $p_{1/2}$ spinor is comprised of both σ and π components and, for this reason, is not an optimum bonding orbital. In a very simple approximation, one of us made calculations [4] assuming promotion of the electron from a $p_{1/2}$ spinor to a $p\sigma$ orbital which is $\frac{1}{3} p_{1/2}$, $\frac{2}{3} p_{3/2}$; for Tl this promotion requires 0.64 eV. This assumption of full promotion was obviously an oversimplification. We are presently carrying out fully relativistic electronic structure calculations for TlH and Tl_2 to determine the actual bonding orbitals under these conditions. If the thallium atom is bonded to a hydrogen atom where only σ bonding is possible, an unchanged $p_{1/2}$ spinor on Tl will yield only 1/3 of a normal σ bond. Very recently Pyper [5] has pointed out that the remaining π component of the $p_{1/2}$ spinor will interact with the H atom in a manner which he calls an "orthogonal triplet bond". He estimates an orthogonal triplet bond to have half the strength of a normal σ bond; hence he asserts that the bond in a TlH molecule (without any promotion of the $p_{1/2}$ spinor on Tl) would have 2/3 the strength of a normal σ bond between those atoms.

Since we had just completed calculations for TlH [6] when Pyper's paper was published, and our programs allow a test of his model; we have carried out the appropriate calculations and report them below.

2. Calculations

Our program for relativistic calculations of molecular properties is based on a frozen-core, effective-potential method for the very heavy atoms. In this case we consider explicitly the outer 13 electrons ($5d_{3/2}^4$, $5d_{5/2}^6$, $6s_{1/2}^2$, $6p_{1/2}$) on Tℓ with the remainder in the frozen core. The molecular calculations are in the multiconfiguration self consistent field (MCSCF) approximation and are formulated in the ω-ω coupling appropriate where spin-orbit energies are large. While the exact evaluation of the basis set is complicated [6], it is essentially "double zeta". These methods are described in detail elsewhere [6-8]; the approximations have been subjected to appropriate tests and found to be quite good. While the 5d and 6s electrons were considered explicitly, they are also essentially core electrons only slightly distorted at normal bond distances.

In our recent calculations for TℓH, a partial promotion from $p_{1/2}$ to $p_{3/2}$ was allowed for the valence electron on thallium. In order to test Pyper's suggestion that a substantial bond will form even in the absence of such a promotion, we have repeated our earlier two-configuration calculations using the same effective potentials and basis functions as before, except for the absence of the $p_{3/2}$ basis spinors on thallium. Our molecular wavefunctions are considerably more flexible than the valence-bond function implied by Pyper's equation. Our two-configuration expression allows optimum ionic character at bonding distances, together with proper dissociation to ground state atoms. Furthermore, the double-zeta representation allows considerable flexibility in the radial functions. None of these factors should have any adverse effect on the orthogonal triplet interaction and may even favor it. The only difference between our present and earlier calculations

is in the absence or presence of $p_{3/2}$ basis spinors on Tℓ.

In order to define a normal sigma bond for TℓH we carried out a third calculation in which complete basis set flexibility was allowed, but in which the spin-orbit effect was suppressed by appropriately averaging the relativistic effective potentials (the mass-velocity and other relativistic effects were left intact). This eliminates the promotion energy between the $p_{1/2}$ and $p_{3/2}$ atomic spinors and thereby allows a "normal" sigma bond to form.

The dissociation curves obtained from these three calculations are shown in Figure 1 and in Table I. Also included in the table is the thallium $p_{3/2}$ to $p_{1/2}$ electron population ratio for the bonding spinor from our earlier calculations where $p_{3/2}$ participation was allowed.

The double-configuration calculation with $p_{3/2}$ participation yields about 75% of the experimental dissociation energy of 1.97 eV [9]. A five-configuration calculation improves this to about 85%; these are normal results for such calculations which include only part of the electron correlation.

It is clear from Table I and Figure 1 that exclusion of the $p_{3/2}$ participation in the bonding spinor eliminates a large proportion of the bond strength.

3. <u>Discussion</u>

The $p_{3/2}$ to $p_{1/2}$ population ratio, given in Table I as 0.60 at the minimum in the potential, is about the same as was obtained in earlier and more approximate investigations [8,10]. Thus the participation of $p_{3/2}$ on Tℓ is 38% which is intermediate between the value 0% for the ground state atom and 67% for a nonrelativistic p sigma orbital. As

noted elsewhere [6], the radial dependence of the $p_{3/2}$ component differs somewhat from that for the $p_{1/2}$ component so that near the hydrogen nucleus the bond is nearly pure sigma. The bond has considerable ionic character with an electron population on hydrogen of 1.3. Other aspects of the TℓH bond have been discussed previously [6].

The bonding without $p_{3/2}$ participation is best discussed in terms of the characteristics at about 5 bohr — well down the potential curve but beyond the range of strong repulsive effects. Also at this point the ionic character is essentially the same with or without $p_{3/2}$ participation (0.3 extra e^- on H). At 5 bohr the normal sigma bond (i.e., without spin-orbit effect) yields a decrease of 0.0515 a.u. in energy relative to the atomic asymptote, whereas the value with the $p_{1/2}$ spinor (without $p_{3/2}$ mixing) is 0.0190 a.u. Thus the bonding without $p_{3/2}$ participation is 36% of a normal sigma bond. This formulation without $p_{3/2}$ implies one-third of a sigma bond and two-thirds of an "orthogonal triplet bond"; thus the contribution of the two-thirds of an orthogonal triplet bond is only 3% of a sigma bond rather than the 33% estimated by Pyper. For the real bond at 5 bohr with $p_{3/2}$ participation allowed and with the spin-orbit term, we find a bond energy of 0.0321 a.u. or 62% of the full sigma bond. On the very approximate basis of full promotion to the 2/3 $p_{3/2}$, 1/3 $p_{1/2}$ bonding orbital on Tℓ one calculates a bond energy of 0.052-0.024 = 0.028 a.u. which is only 0.004 a.u. less than the correct result in our present general approximation. It is to be expected that the optimum bond will have less than full promotion and a lower energy than that calculated for full promotion.

At the potential minimum the picture is complicated by various distortions related to the repulsive effects which are now substantial.

For example the ionic character without $p_{3/2}$ mixing increases to 44%
at 4.0 bohr (in contrast to 28% with $p_{3/2}$ participation). There are
substantial changes in the radial functions. In particular for the
function without $p_{3/2}$ the effective zeta for hydrogen falls below 0.95
indicating a diffuse hydride-ion-like situation. We suspect that this
diffuse "ionic" character could be replacing the thallium sigma
character lost due to the absence of $p_{3/2}$ basis spinors, and could
easily account for the difference between the bond energy for the
$p_{3/2}$-suppressed wavefunction and that which one would expect from
one-third sigma bonding alone. Regardless of such complications it is
clear from Figure 1 that the potential curve without $p_{3/2}$ participation
is only marginally deeper than one-third that of the normal sigma bond.
From this alone one can conclude that the orthogonal triplet interaction
is not an important factor in bonding in TℓH.

For GaH and InH, the dissociation energies for the $^3\Pi$ terms are
known to be small. Furthermore, there are reported to be potential
maxima in the dissociation curves. Ginter and Battino [11], who made
detailed calculations based on the spectra, suggest that the potential
maxima arise from avoided crossings and, in their words, "that the
zero-order potential curves for both the $^3\Pi$ and $^1\Pi$ states which eminate
directly from ground-state atomic terms are intrinsically unstable".
In other words, they conclude the bonding in the $^3\Pi$ term arises pri-
marily from bonding orbitals involving sp^2 metal atoms. Such states
would dissociate to excited atoms. The avoided crossings connect
these curves based on excited atoms with repulsive potential curves for
$^3\Pi$ states which relate to ground-state atoms. Pyper's orthogonal
triplet is the $^3\Pi$ associated with the ground-state atoms which Battino
and Ginter conclude to be repulsive. Calculations for BH [12,13]

indicate that this characteristic of the $^3\Pi$ term is the same in BH as in GaH and InH.

But even without Battino and Ginter's more detailed arguments, it is clear that the orthogonal triplet interaction is not significantly bonding in GaH and InH. The lowest state of a given symmetry will be represented by the wavefunction (of that symmetry) with the lowest energy. Thus, if the orthogonal triplet wavefunction for GaH, InH corresponded to a bond with half the strength of a normal sigma bond, there would be a $^3\Pi$ term with at least that dissociation energy. If the lowest $^3\Pi$ states are of higher energy and have different bonding wavefunctions, then the energy corresponding to the orthogonal triplet wavefunction must be even higher in energy, i.e., even less bonding.

Pyper prefers to take the highly excited $^3\Pi_r$ terms of CuH and AgH as examples of the orthogonal triplet bond and argues that the closed ns^2 shell interferes for such bonding in group III atoms. But for realistic chemical valence discussion of bonding with a single p-electron there always will be an ns^2 shell present; consequently, the appropriate question relates to the nature of an orthogonal triplet interaction in the presence of an ns^2 shell.

Pyper's identification of terms analogous to a nonrelativistic $^3\Pi$ state in the $p_{1/2}$ - s bonding function is quite correct. But we conclude both from our own calculations for TℓH and from information in the literature that, in the chemically interesting case with an ns^2 shell, the orthogonal triplet interaction, which Pyper asserts to be a significant bond, is instead a very weak interaction. The bonding in

TℓH is modified by relativistic effects, including the substantial energy required for partial promotion from $p_{1/2}$ to $p_{3/2}$ of the valence orbital on Tℓ, but the orthogonal triplet interaction is not an important aspect.

Acknowledgment

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Table 1. Calculated energies (in a.u.) for TℓH on three bases.

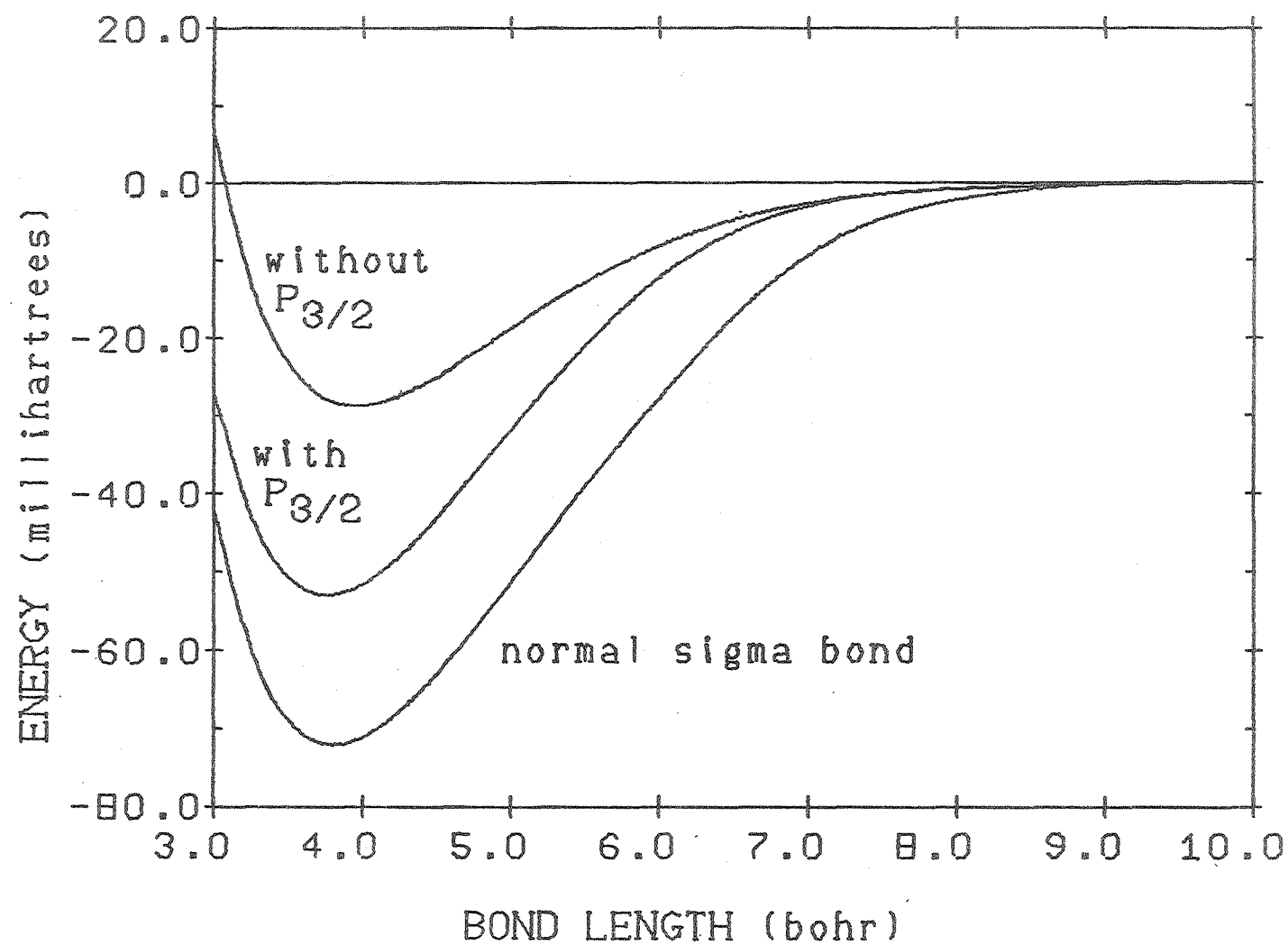| R(a.u.)	Without $p_{3/2}$ Mixing	With $p_{3/2}$ Mixing	Mixing Ratio $p_{3/2}/p_{1/2}$	Without Spin-orbit
3.0	+0.0059	−0.0275	0.59	−0.0425
3.25	−0.0134	−0.0434	0.59	−0.0603
3.5	−0.0234	−0.0510	0.60	−0.0691
3.75	−0.0279	−0.0532	0.60	−0.0721
4.0	−0.0288	−0.0519	0.59	−0.0713
4.5	−0.0252	−0.0434	0.54	−0.0632
5.0	−0.0190	−0.0321	0.42	−0.0515
6.0	−0.0083	−0.0125	0.19	−0.0279
8.0	−0.0009	−0.0010	0.00	−0.0023
10.0	−0.0001	−0.0001	0.00	−0.0002
15.0	0.0000	0.0000	0.00	0.0000

Figure 1. TℓH dissociation curves computed with and without
$P_{3/2}$ mixing, and with the spin-orbit splittings
suppressed (normal sigma bond).